Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **JUN 2009**	2. REPORT TYPE	3. DATES COVERED **00-00-2009 to 00-00-2009**

4. TITLE AND SUBTITLE **Silicon Carbide as a Platform for Power Electronics**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Naval Research Laboratory,4555 Overlook Avenue SW,Washington,DC,20375**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	4	

tion. Gross *et al.* show that the method is sufficiently sensitive to distinguish the charge states of individual adatoms decoupled from the substrate by an ultrathin insulating ionic layer. Therefore, the authors can distinguish a neutral from a positively or negatively charged atom.

This achievement has tremendous consequences for the field of molecular electronics. It remains extremely difficult to electrically connect single molecules and to measure their electrical conductance. Most current lithography methods (*8*) yield metallic wires some tens of nanometers in diameter, much larger than the diameter of the molecules (typically on the order of 1 nm). This problem can be overcome by using geometries such as break junction experiments (*9*) and lifting up molecular or metallic wires by an STM tip (*10*). However, these methods do not allow spatial and electrical information to be obtained simultaneously without destroying the molecular structure. The crucial advance of Gross *et al.* is to perform their experiments without wiring the object of interest. This approach allows individual charges to be added to or removed from an atom and furthermore enables the direct measurement of the charge state.

The method of Gross *et al.* can be extended to molecules or molecular networks, where charges can be added or removed at specific sites of the molecules (redox sites). Subsequently, the whole molecule or molecular network can be characterized by Kelvin probe force microscopy or optical techniques to investigate the charge transport or conformation changes. In a recent study, Glatzel *et al.* demonstrated the contacting of single molecular structures assembled on insulating surfaces by metal clusters as well as their distinction by local Kelvin probe force microscopy measurements (*11*). By combining this approach with single atoms connected directly to the molecular structure, the charge transport can in principle be investigated without applying an external electrical current. The AFM tip can alter the charge state of one of the metallic terminals (see the figure). Afterward, the change of the charge states of the other terminals can be measured by Kelvin probe force microscopy, elucidating the propagation of charges in the molecule or molecular network. Comparison with theoretical models will give the opportunity to learn more about the energy landscape of the molecules, which is probed by single injected electrons.

A change of atomic or molecular charge state is a central feature in many chemical reactions. Combining the redox sites—that is, the metal atoms or clusters connected to the molecular structures—with probe microscopy therefore provides a novel tool for manipulating individual molecules and for performing chemical, electrochemical, or photochemical reactions with a high degree of control. In combination with optical excitation (*12*), it will allow absorption and charge generation to be measured at the molecular scale. This method is thus not only of interest for molecular electronics, but also for catalysis, material synthesis, and photovoltaics.

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10.1126/science.1175869

MATERIALS SCIENCE

Silicon Carbide as a Platform for Power Electronics

Methods for growing large, defect-free silicon carbide crystals have enabled the fabrication of devices that can operate at high power.

C. R. Eddy Jr. and D. K. Gaskill

For high-voltage, high-current devices that can be operated at elevated temperatures, silicon carbide (SiC) has been the material of choice. Efforts to produce single-crystal SiC began 30 years ago, but intrinsic problems in growing high-quality single-crystal boules free of micropipe defects—micrometer-scale pinholes created by dislocations—have only recently been overcome. A series of developments in crystal growth have made large-area, high-quality SiC substrates readily available for applications such as high-frequency transmitters and solid-state white lighting. Additional reductions in defects in the active region of devices have been achieved through epitaxial approaches, in which single-crystal layers are grown on the substrate. SiC is now poised as the linchpin to "green energy" that will replace less energy-efficient switches now based on silicon technology.

The choice of a semiconductor for switching electrical currents on and off depends on the operating voltage and how much current must be controlled. Silicon is an excellent material for the low-power transistors used in microelectronics, but for high currents and voltages, its implementation becomes complex and thermal management issues arise. The fundamental properties of SiC make it a better choice under these conditions.

One reason why SiC has been of fundamental interest to materials scientists is that it exists in more than 200 stacking modifications (polytypes) (*1*). With the advent of the vapor-phase Lely growth process in 1955, small, high-quality SiC single-crystal platelets (about 1 cm^2 in area) could be made (*2*). The most readily synthesized hexagonal polytypes, 4H and 6H, have a large indirect band gap (~3.2 eV) and a large breakdown electric field (2 MV cm^{-1}), as well as high electron mobility (900 $cm^2\ V^{-1}\ s^{-1}$) and thermal conductivity (400 W $m^{-1}\ K^{-1}$). Given these properties, SiC power switches should have performance figures of merit 10 to 100 times those of silicon switches.

The growth of SiC crystals presents many challenges. A SiC boule is typically grown by transporting its physical vapor to a seed crystal chosen to be as defect-free as possible. This

U.S. Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375, USA. E-mail: david.gaskill@nrl.navy.mil; charles.eddy@nrl.navy.mil

process requires extremely high temperatures (~2200°C) (*3*). Furthermore, impurities must be avoided both in the SiC feedstock and in the graphite insulation used in the growth reactor. Variations in the atomic ratio of Si to C in the vapor phase that arise from feedstock granularity must be minimized during growth. Radial and axial thermal profiles in the reactor and boule must be controlled to avoid polycrystallinity, grain boundary formation, and other defects in the lattice. Because the understanding of materials properties at these extreme temperatures is incomplete, boule growth modeling efforts must be based on extrapolated parameters. Last, all of the challenges of growing good-quality SiC boules increase as the diameter of the substrate increases.

The challenges do not end once the single crystal is grown, because the lattice structure of the boule tends to replicate any defects in the starting seed crystal. Defects include basal plane dislocations (BPDs) that shift atom locations within that plane, and threading screw dislocations (TSDs) that shift atoms out of the basal plane and stack them in a spiral arrangement. Micropipes are larger-scale screw dislocations that create a pinhole through the substrate. These extended defects can occur with such high densities (up to 10,000 per square centimeter) that there is no usable area on the crystal surface to fabricate a working device.

Fortunately, at the high growth temperatures used, most dislocations have some mobility, and their interactions can cause them to cancel or "annihilate." The higher-quality part of the boules can then be used as better seed crystals. This slow but steady improvement in seed crystals and boule growth control has made larger-diameter, higher-quality wafers commercially available. Five years ago, only 50-mm-diameter SiC substrates were available, and today, 100-mm-diameter wafers are available (*4*). Expansion to 150-mm diameter would lead to substantial cost reductions because modern compound semiconductor processing equipment is designed for these larger wafers.

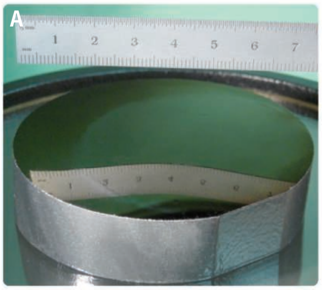
The bigger payoff that has occurred during this evolution in size has been a reduction in defects. In particular, the "killer defect" that has hampered the development of SiC devices, the micropipe, has been practically eliminated (*5*); commercially available wafers now have micropipe densities less than 1 cm^{-2} and are, in some cases, "micropipe free."

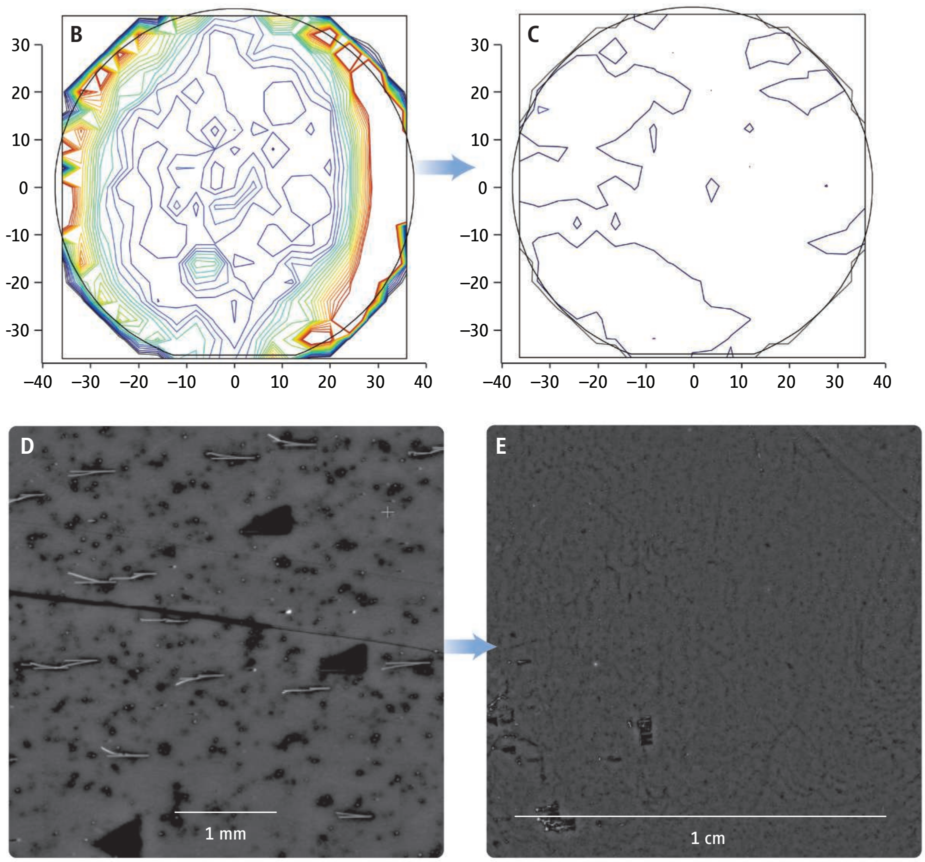
The current focus is on the reduction of BPDs, which are now the most important defects to eliminate, as well as TSDs. BPDs have deleterious effects on device performance, particularly for high-voltage bipolar devices. The 1c type of TSD has been linked to leakage in the common vertical device structures used in high-voltage power switches and diodes.

The BPDs propagate from the substrate into the epitaxial layers because the substrates must be offcut from the basal plane in order to maintain polytype control. The TSDs will propagate into the epitaxial device region independent of any offcut. In either case, it is highly desirable to reduce the densities of the extended defects in the active epitaxial layers. Reducing BPDs and TSDs to the desired level through boule manufacture alone will require extremely tight control on thermal gradients over larger dimensions at these extreme growth temperatures. Complementary approaches to develop epitaxial methods that can reduce BPD and TSD densities early in the growth process, and keep them out of the active regions of power devices, have shown considerable promise.

Using two epitaxial methods compatible with the manufacturing process (*6*, *7*), BPD densities have been reduced to the desired level of <1 cm^{-2}, although epitaxial approaches have not yet been implemented in the fabrication of device structures. Epitaxial approaches can also reduce propagation of TSDs from the substrate to the epilayers (*8*) and can keep such defects out of the active region of devices. Current efforts aim to reduce BPDs and TSDs to densities at or below 1 cm^{-2} both in boule manufacture and in epitaxial growth.

With the recent advances in SiC substrate quality, high-performance radio-frequency





Progress in the development of SiC substrates. (**A**) SiC boule growth has advanced during the past 5 years to permit larger-diameter wafers with vastly improved quality [a 3-inch (76-mm) boule is shown]. (**B** and **C**) X-ray diffraction symmetric reflection peak width maps, ranging from 12 (black) to 120 arc sec (red) are shown in millimeters from the wafer center. Reduced peak widths in (C) demonstrate recent improvements in crystalline quality and uniformity. (**D**) Basal plane and threading screw dislocation reduction (white lines and dots, respectively, in the ultraviolet photoluminescence image) are detrimental to electronic device performance. (**E**) Recent bulk and epitaxial growth approaches have combined to yield sufficiently large (1 cm^2) areas free of basal plane dislocations (*6*, *7*).

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devices, based either on SiC or on gallium nitride grown epitaxially on SiC, have become practical for use in advanced communications and radar systems. In addition, SiC wafers have been shown to be an effective vehicle for realizing large-area graphene films that may find application in terahertz devices and next-generation microprocessors.

The elimination of micropipes, when accompanied by reductions in BPDs and TSDs, suggests that high-voltage, high-current SiC electronic switches with increased efficiencies may be on the horizon. These types of devices will have a direct impact on energy conversion and distribution systems, as well as on electromechanical conversion processes that now rely on less efficient technologies.

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10.1126/science.1168704

CANCER

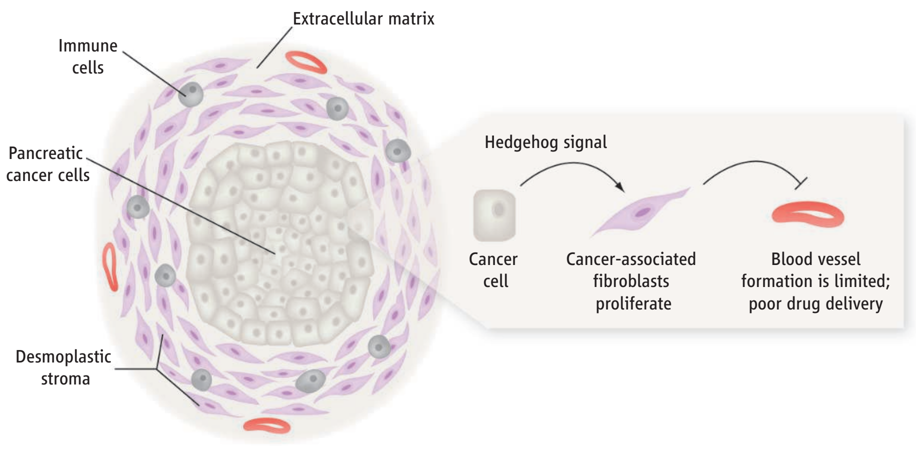
Breaching the Cancer Fortress

Pancreatic tumors are poorly vascularized, suggesting that new therapeutic strategies are needed.

Peter Olson and Douglas Hanahan

The predominant and invariably lethal form of pancreatic cancer—ductal adenocarcinoma—is characterized by an enveloping fibrotic stroma of excessive connective tissue and cells that forges rock-hard tumors. These tumors are refractory to essentially all therapies; gemcitabine, the standard-of-care chemotherapeutic drug, extends survival by only a few weeks. It has long been surmised that these pathological and clinical features are interconnected. On page 1457 in this issue, Olive *et al.* (*1*) confirm this notion, showing that cancer-associated fibroblasts in pancreatic ductal adenocarcinoma are responsible for a poorly vascularized architecture that imposes a barrier to drug delivery. Removing these fibroblasts stimulated the formation of new blood vessels (angiogenesis), improved drug delivery, and extended life span in a de novo mouse model of the disease. This study defines biophysical properties endowed by the tumor microenvironment that contribute to its therapeutic intractability and raises new questions about the role of the microenvironment in the development of this uncontrollable cancer.

Olive *et al.* noted that tumors from a de novo mouse model of pancreatic ductal adenocarcinoma responded poorly to gemcitabine, mimicking the clinical experience. However, transplanted tumors that were generated from cell lines derived from these tumors were remarkably sensitive to the drug. Transplanted tumors lacked the abundant fibrotic response present in human and de novo mouse tumors, in which epithelial cancer cells are surrounded by large swathes of activated fibroblasts, immune cells, blood vessels, and extracellular matrix components—a "fortress" collectively referred to as the desmoplastic stroma (see the figure) (*2*). The tumor microenvironment is thought to promote an ample vasculature to fuel tumor growth. However, in the de novo mouse model, blood vessels were sparse, only partially functional, and were physically separated from the epithelia by stroma. Two imaging techniques confirmed that blood flow was low in these tumors, and delivery of the naturally autofluorescent anticancer drug doxorubicin was decreased compared with delivery to transplanted tumors or normal tissue.



Barrier to drug delivery. In pancreatic ductal adenocarcinoma, cancer cells are surrounded by a fortress of desmoplastic stroma composed of cancer-associated fibroblasts and inflammatory cells along with copious amounts of extracellular matrix components. This assemblage impedes angiogenesis, limiting drug delivery. (**Inset**) The secreted factor Hedgehog sustains this stromal environment. Inhibition of Hedgehog signaling eliminates cancer-associated fibroblasts, thus increasing angiogenesis and vascular delivery of chemotherapeutic drugs.

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Cancer-associated fibroblasts promote tumor growth and angiogenesis in other tumor types (*3*–*5*). Surprisingly, cancer-associated fibroblasts in pancreatic ductal adenocarcinoma were responsible for the sparse vasculature and poor drug delivery. These cancer cells signal in a paracrine fashion to fibroblasts via the secreted factor Hedgehog. Olive *et al.* treated mice with de novo tumors with a pharmacological Hedgehog inhibitor alone and in combination with gemcitabine. There was equivocal survival benefit with Hedgehog inhibitor therapy, and only a few weeks of added survival with the combination. Nevertheless, the Hedgehog inhibitor largely eliminated fibroblasts, while vascular endothelial and other cell types proliferated. The results suggest that cancer-associated fibroblasts in pancreatic ductal adenocarcinoma limit the formation of new blood vessels, with

Comprehensive Cancer Center, Diabetes Center, and Department of Biochemistry and Biophysics, University of California, San Francisco, San Francisco, CA 94143–0534, USA. E-mail: polson@diabetes.ucsf.edu; dh@ucsf.edu